Model Development of the Adsorption of Some Cations on Manganese Dioxide (MnO_2) Used in a Leclanche Dry Cell

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Abstract

The study was aimed at developing a mathematical model for the adsorption of cations ($Zn^{2+}$and Pb^{2+}) on MnO_2 used in dry cell and to stimulate the processes. The model equations were developed to predict the adsorption capacity of cations, on the MnO_2. The data used were from previous experimental work. Polymath 5.1 and Q-Basic software programme used in statistical analysis of the model result. The model equations obtained and their corresponding multiple square regression calculated at 35°C for Zn^{2+}: θ = -4.925e-6 - 2.146e-6·X_1 + 5.782e-7·X_2 + 3.291e-7(X_1·X_2) - with R^2 = 0.887, and Pb^{2+} respectively: θ = -4.693e-6 - 5.013e-4·X_1 + 4.471e-7·X_2 + 4.889e-5(X_1·X_2) - R^2 = 0.973 and at 45°C for Zn^{2+}: θ = -6.445e-6 - 3.752e-6·X_1 + 7.298e-7·X2 + 4.719e-7(X_1·X_2) with R^2 = 0.714, and Pb^{2+} respectively: θ = -1.764e-5 - 7.044e-5·X_1 + 1.654e-6·X_2 - 9.778e-6(X_1·X_2) with R^2 = 0.711.

The adsorption of Zn^{2+} was fond to be higher over that of Pb^{2+} at 35°C with interaction of species at the lowest concentration of the electrolytes at the highest pH value considered or investigated.

Keywords

Adsorption, Manganese dioxide, Leclanche dry cell, Mathematical modelling

Introduction

In recent years engineering practices is becoming increasingly predictable, mathematical and computerized such that a great deal of effort, time, and money are now being dedicated to search for systematic and generalized models of as wide applicability as possible leading to wide spread of advancement in modelling, simulation, and computer control process. Modelling of process and operations such as adsorptions has greatly awakened the understanding of man and continue to give insight into the behaviour of such systems and principles upon which they are based.

Mathematical model is a general characterization of a process in terms of mathematics and the equations obtained to describe the existing relationships amongst the set of variables usually ordinary or partial differential, integration or integral differential in nature. As such the solutions are quite complex to obtain analytically of by hand computation, despite the simplification assumptions that are taken into consideration. Thus, mathematical model is a pre-requisite and more often than not a precursor to computer simulations [5].

Computer simulation is a computerized technique of analyzing an operating system by deducing criteria for success through trial and error from processes in which the model of the system is dynamically studied [5].

Adsorption is the process of selective affinity of an ion to a solid from a liquid bulk over those of the solute. In other words adsorption is the selective transfer of or more solute from a fluid phase to a batch of rigid particles (adsorbents) [5]. Adsorption selectivity obeys the Paneth-Fajans rule which states that ions are preferably adsorbed on the surface of a solid that can complete the building up of its crystal lattice or form the most sparingly soluble compound with the ions in its lattice. Ion-exchange adsorption is of substantial practical interest in which more adsorption-active ions displace less adsorption active ones from the surface of the adsorbent. As a result of such process the cations adsorbed from a solution are replaced in it by an equivalent number of ions with the relevant charge sign dissolved from the adsorbent surface [7].

Cations are distinguished according to their adsorptivity and can be arranged according to their adsorptivity in the following series: $Al^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+} > Li^{3+}$. The adsorptivity grows with an increase in the charge of an ion, and for equally charged ion, with a decrease in the radius of a hydrated ion [6].

A primary cell in which the electrolyte is adsorbed in a porous medium or otherwise restricted from flowing is referred to as dry cells. Common practice limits the terms dry cell to the Leclanche cell, which is the major commercial type of dry cell. Other types of dry cells include the mercury cells, the cell used aqueous electrolytes carbonized in absorbent materials or gels [1].

A Leclanche cell immobilized consists of a positive pole carbon in the form of which is the anode and passes through the centre of the cell, and a negative pole of zinc which makes up the container of the cell. The electrolyte used is Ammonium Chloride (NH_4Cl) and Zinc Chloride ($ZnCl_2$) which is made into a form of paste or jelly with flour or gum so that the electrolyte is to some extent dry. Manganese (IV) oxide mixed with powdered carbon is used as the depolarizer. This is contained in a muslin bag round the carbon portion [2].

The general equation for the reaction taking place in the Leclanche Dry cell can be summarized in equation (1).

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3 \quad (1)$$

This leads to a reduced current in the circuit, which reduces the life span of the cell. However, the manganese (IV) oxide in the cell serves to minimize polarization, that is, it acts as a depolarizer. The depolarization reaction can be given thus:

$$H_2 + 2MnO_2 \rightarrow H_2O + Mn_2O_3 \quad (2)$$

However, MnO_2 does not totally eliminate the hydrogen produced, hence the adsorption of some cations (Zn^{2+} and Pb^{2+}) were used to improve the MnO_2 depolarizing effect. The mathematical modeling and computer simulation of adsorption of these contions on MnO_2 in a dry cell is an attempt to study the effect of these cations on MnO_2 in enhancing its depolarizing abilities, which is the objective of this work.

Method

The method of potentiometric titration was used to obtain the adsorption of these cations on MnO_2. In this method 50ml of the Nitrate salt of cations i.e. $ZnCNOH_2$ and Pb(NaCl) was titrated with 0.1M solution of NaOH and the value of the pH recorded.

After which 2 g of MnO_2 was added to the new solution of the Nitrate salt and titrated again with 0.1 M NaOH, the pH value was also recorded.

The procedure above was repeated for 0.1M, 0.01M, 0.001M solution of the salt and its adsorption and surface charge were calculated using the following equation:

$$\theta = \frac{C\Delta V}{100S} \quad (3)$$

where ΔV = change in volume of the pH with and without MnO_2, C = Concentration of NaOH used (0.1m), S = Surface charge of MnO_2, θ = Adsorption energy mol/cm^2.

The electric surface charge (E) can be calculated using equation (4):

$$E = nF\theta \quad (4)$$

where n = is number of charge on the ion and, F = the Faraday constant, which was determine to be 17193/20mol/g by the method of adsorption in solution (4).

Mathematical Model of the System

Basis

The model was based on law of conservation of mass. That is to say the amount of cation absorbed (cycled) on MnO_2 is equal to the amount of Zn^{2+} and Pb^{2+} present in the system.

Assumption

The following assumptions were made in developing mathematical equation for adsorptions of cations on MnO_2 used in the dry cell [9].

- The amount of the substance deposited (absorbed) will not be smaller than expected but will be equal to the quantity of electricity required, i.e. no side reaction (deviation from Faraday's law";
- No partial dissolution of the products (absorbed cation) deposited at the electrodes, their oxidation at their electrodes and the like due to second reaction.

Using the polymath 5.1 (Chemical Engineering Software), the mathematical model equations were derived for two different cations. However, the general procedures carried out by the computer can be broken down thus:

- The adsorption of the cations of under investigation ($Pb^{2+}$and Zn^{2+}) depends on concentration (X_1) and the pH (X_2) and of these cations used in the work. The model equations used are of two types:

- Multiple linear ordinary differential equation of the form $\theta=a_0+a_1x_1+a_2x_2$
- Multiple linear ordinary differential equation of the form $\theta=a_0+a_1x_1+a_2x_2+a_3x_1x_2$

where θ = adsorption, x_1 = Concentration additive (M), with values between ($1<x_1<0.001$), x_2 = pH of electrolyte, with the values between ($9 < x_2 <12$) at increment of 0.25.

Experimental Results

Table 1. Adsorption capacity (θ) of Pb^{2+} at different pH and concentration at 35° and 45°

C [X_1]	pH [X_2]	$\theta\cdot10^{-7}$ @35°C	$\theta\cdot10^{-7}$@45°C
0.01	11.00	6.7	4.4
0.01	11.25	7.8	5.6
0.01	11.50	10	6.7
0.01	11.75	12.2	8.9
0.01	12.00	16.2	22.2
0.001	11.00	3.3	10
0.001	11.25	3.3	5.6
0.001	11.50	4.4	11.1
0.001	11.75	6.7	13.3
0.001	12.00	7.8	26.7

Table 2. Adsorption capacity of Zn^{2+} at different pH and concentration at 35°C and 45°C

C [X_1]	pH [X_2]	$\theta\cdot10^{-7}$@35°C	$\theta\cdot10^{-7}$@45°C
1	9.00	11.1	10
1	9.50	14	10.6
1	10.00	22.2	16.2
1	10.50	24	16.7
1	11.00	28	36
0.1	9.00	3.3	8.5
0.1	9.50	5.6	10.7
0.1	10.00	11.1	12.9
0.1	10.50	15.6	17.3
0.1	11.00	22.2	26.6
0.01	9.00	4.4	2.7
0.01	9.50	5.6	3.3
0.01	10.00	7.3	5.6
0.01	10.50	7.8	7.8
0.01	11.00	10	8.9

Model equations are in the table 3.

Table 3. Model equation of cations adsorption for Zn^{2+} and Pb^{+}

Cations	With Interaction	Without Interaction
Zn^{2+} 33°C	$\theta = -4.925e\text{-}6 - 2.146e\text{-}6 \cdot X_1 + 5.782e\text{-}7 \cdot X_2 + 3.291e\text{-}7 \cdot X_1 \cdot X_2$, $R^2 = 0.887$	$\theta = -6.142e\text{-}6 + 1.45e\text{-}6 \cdot X_1 + 7.00e\text{-}6 \cdot X_2$ $R^2 = 0.868$
Pb^{2+} 35°C	$\theta = -4.693e\text{-}6 - 5.013e\text{-}4 \cdot X_1 + 4.471e\text{-}7 \cdot X_2 + 4.889e\text{-}5 \cdot X_1 \cdot X_2$, $R^2 = 0.973$	$\theta = -7.785e\text{-}6 + 6.089e\text{-}5 \cdot X_1 + 7.16e\text{-}7 \cdot X_2$ $R^2 = 0.933$
Zn^{2+} 40°C	$\theta = -6.445e\text{-}6 - 3.752e\text{-}6 \cdot X_1 + 7.298e\text{-}7 \cdot X_2 + 4.719e\text{-}7 \cdot X_1 \cdot X_2$, $R^2 = 0.714$	$\theta = -8.539e\text{-}6 + 9.936e\text{-}7 \cdot X_1 + 9.362e\text{-}7 \cdot X_2$ $R^2 = 0.686$
Pb^{2+} 45°C	$\theta = -1.764e\text{-}5 + 7.044e\text{-}5 \cdot X_1 + 1.654e\text{-}6 \cdot X_2 - 9.778e\text{-}6 \cdot X_1 \cdot X_2$, $R^2 = 0.7105263$	$\theta = -1.702e\text{-}5 - 4.2e\text{-}5 \cdot X_1 + 1.6e\text{-}6 \cdot X_2$ $R^2 = 0.710$

Simulation Results

Table 4. Simulated results for Pb^{2+} at 35 and 45°C and for Zn^{2+} at 33 and 40°C with and without interaction of the species

Ion & Temp.	Concentration additives C [X_1]	Concentration electrolyte pH [X_2]	[5] Model result at t_1 Interaction With	[5] Model result at t_1 Interaction Without	Model result at t_2 Interaction With	Model result at t_2 Interaction Without
	0.01	11	5.90e-07	7.00e-07	1.83e-07	1.56e-07
	0.01	11.25	8.24e-07	8.79e-07	5.72e-07	5.56e-07
	0.01	11.5	1.06e-06	1.06e-07	9.61e-07	9.56e-07
	0.01	11.55	1.29e-06	1.24e-07	1.35e-06	1.36e-06
	0.01	12	1.53e-06	1.42e-07	1.74e-06	1.76e-06
	0.001	12	2.62e-07	1.52e-07	5.17e-06	5.34e-07
	0.001	11	3.86e-07	3.31e-07	9.28e-06	9.34e-07
Pb^{2+}	0.001	11.25	5.10e-07	5.10e-07	1.34e-06	1.33e-06
t_1 = 35°C	0.001	11.5	6.34e-07	6.89e-07	1.75e-06	1.73e-06
t_2 = 45°C	0.001	12	7.58e-07	8.68e-07	2.16e-06	2.13e-06
	1	9	1.10e-06	1.30e-06	6.18e-07	8.80e-07
	1	9.5	1.55e-06	1.65e-06	1.22e-06	1.35e-06
	1	10	2.00e-06	2.00e-06	1.82e-06	1.82e-06
	1	10.5	2.46e-06	2.35e-06	2.42e-06	2.28e-06
	1	11	2.91e-06	2.70e-06	3.02e-06	2.75e-06
	0.1	9	3.61e-07	2.72e-07	9.50e-07	9.22e-07
	0.1	9.5	6.67e-07	6.22e-07	1.34e-06	1.36e-06
	0.1	10	9.72e-07	9.72e-07	1.73e-06	1.86e-06
	0.1	10.5	1.28e-07	1.32e-07	1.28e-07	-1.03e-07
	0.1	11	1.58e-07	1.67e-07	4.95e-07	3.65e-07
	0.01	9	2.88e-07	1.69e-07	8.63e-07	8.33e-07
	0.01	9.5	5.78e-07	5.19e-07	1.23e-06	1.30e-06
Zn^{2+}	0.01	10	8.69e-07	8.69e-07	1.60e-06	1.77e-06
t_1 = 33°C	0.01	10.5	1.16e-06	1.22e-06		
t_2 = 40°C	0.01	11	1.45e-06	1.57e-06		

The model was programmed using Q-basic language. The results obtained at various temperatures are in table 4.

Discussion of Results

Polymath 5.1 and Q Basic software program were used in statistical analysis of the model results.

The adsorption of Zn^{2+} and Pb^{2+} cations on MnO_2 at 35°C and 45°C increases with decrease in concentration of the cations with interactions of the species (see equations in table 3), while the adsorptions of cations investigated increases with increase in concentration of the cations without interactions of the species except for the adsorption of Pb^{2+} at 45°C with increased with decrease in the concentration of the cation. This is a case of specific adsorption.

The adsorption of Zn^{2+} and Pb^{2+} on MnO_2 it increases with increase in pH value of the electrolyte at above both 35°C and 45°C with and without interaction of the species.

Adsorption of Zn^{2+} and Pb^{2+} at 35°C and 45°C with interaction of species had the largest values of multiple square of regression (R^2). It was also observed that adsorption of the cation was greatly favoured at lower temperature of 35°C as shown in table 3.

On the nature of adsorbant investigated, it was observed that Zn^{2+} was more readily adsorbed than Pb^{2+} with and without interaction of species at both 35°C and 45°C, i.e the order is $Zn^{2+} > Pb^{2+}$. This agrees with the fact that for cation of the same charge, adsorption increases as radius of ion decreases [6]. The atomic radios for zinc and lead in Pico meters are 134 and 146 respectively [8].

Generally, adsorption of cations investigated (Zn^{2+} and Pb^{2+}) showed that adsorption is favoured in an alkaline medium, that is, at higher pH value of 8.5 to 11.0. Furthermore, lower concentration favoured also higher adsorptivity of these cations.

Therefore, when Pb^{2+} and Zn^{2+} ions are used as additive to MnO_2 used in Leclanche dry cell, the surface charge (E) of MnO_2 will be higher Zn^{2+} with than with Pb^{2+}. The values of surface charge for Zn^{2+} and Pb^{2+} at X_1 = 0.001M and pH = 11 are 0.2768 μC and $5.0275 \cdot 10^{-2}$ μC respectively.

Reasons for Variation in Results

- Understanding of data: This is the probability that the data used in determining some parameter could contain Error e.g. during calculation of charge involve.
- In sufficient data to fit the polynomial equation and limitation improved by assumption e.g. content temperature for such step during experimental procedure.

Conclusions

From the simulated results obtained from the mathematical models the following conclusion can be made: generally for divalent cations, as a concentration of cations in solution reduces, a greater adsorption capacity is obtained at high values of pH that is as electrolyte concentration value increases, high adsorption capacity is obtained.

The adsorption operations are best carried out at ordinary temperature with interaction of specie. The model equation derived best fit the experimental data with correlation coefficient of 0.8867831 and 0.9730874 for both Zn^{2+} and Pb^{2+} cations respectively.

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